

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 019 438**  
**A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 80301534.6

(22) Date of filing: 09.05.80

(51) Int. Cl.<sup>3</sup>: **C 08 L 67/02**

**C 08 K 5/12, C 08 J 5/18**  
**B 32 B 27/36, B 32 B 27/08**  
**B 32 B 27/10, B 65 D 65/40**  
**/(C08L67/02, 29/04)**

(30) Priority: 11.05.79 US 38094

(43) Date of publication of application:  
26.11.80 Bulletin 80/24

(84) Designated Contracting States:  
AT BE CH DE FR GB IT LI NL

(71) Applicant: **CLOPAY CORPORATION**  
**Clopay Square**  
**Cincinnati, Ohio 45214(US)**

(72) Inventor: **Cancio, Leopoldo V.**  
**5880 Turpin Hills Drive**  
**Cincinnati, Ohio 45214(US)**

(72) Inventor: **Miller, Gerald W.**  
**2165 Cablecar Drive**  
**Cincinnati, Ohio 45214(US)**

(72) Inventor: **Wu, Pai-Chuan**  
**9564 Linfield Drive**  
**Cincinnati, Ohio 45214(US)**

(74) Representative: **Allen, Oliver John Richard et al,**  
**Lloyd Wise, Tregear & Co. Norman House 105-109**  
**Strand**  
**London, WC2R 0AE(GB)**

(54) Polyester compositions for gas and moisture barrier materials, barrier materials formed from said compositions and a container formed from a layer of said barrier material.

(57) Polymer blends of

- (a) a polymer selected from the group consisting of a poly(ester) and copolymers thereof, and  
(b) a polymer selected from the group consisting of poly(vinyl alcohol) and copolymers thereof, may be fabricated into barrier packaging materials having very low permeabilities to oxygen, other fixed gases and moisture.

**EP 0 019 438 A1**

Polyester Compositions For Gas and Moisture Barrier  
Materials, Barrier Materials Formed From Said  
Compositions and a Container Formed From a Layer Of  
Said Barrier Material

This invention relates generally to a composition  
for gas and moisture barrier materials.

Poly(vinyl alcohol) and its copolymers are known to  
possess low permeabilities to gases. However, the use of  
5 these materials for packaging in their native form restricts  
their use in moisture-containing atmospheres due to the  
presence of the many hydroxyl groups in the polymer.  
Further, permeabilities to oxygen, carbon dioxide and  
other fixed gases are very low, and increase exponentially  
10 as a function of the relative humidity. Polyolefin  
copolymers exhibit the sensitivity to humidity to a lesser  
degree. Commercial packaging and other barrier materials  
require low permeabilities to gases and moisture. A  
recent proposal to overcome this problem was disclosed  
15 in U.S. Patent No. 4,003,963 by using certain mixtures of  
poly(vinyl chloride) and poly(vinyl alcohol) copolymers.  
The vinyl chloride polymer containing no carboxyl groups  
was blended with about 10-30 per cent by weight, based on  
the weight of vinyl chloride polymer, of an ethylene/vinyl  
20 alcohol copolymer containing greater than about 61 weight  
per cent of 50 mole per cent of vinyl alcohol as comonomer.

Another approach to the problem is disclosed in U.S.  
Patent No. 3,585,177. According to this patent, a lower  
alpha olefin/vinyl alcohol copolymer is prepared having a  
25 residual ester content below 3 per cent and an olefin

content between 5 and 40 per cent by weight. Differential thermal analysis was used to show that the copolymers have a single narrow endotherm with a melting range of less than 30°C. Other combinations in the art of barrier compositions are blends of inexpensive materials with those materials having good barrier properties. Such possibilities are limited by the incompatibilities of such blends.

According to the present invention we provide a composition for gas and moisture barrier materials comprising a blend of

- a) a polymer selected from the group consisting of a poly(ester) and copolymers thereof, and
- b) a polymer selected from the group consisting of poly(vinyl alcohol) and copolymers thereof.

The present invention is predicated in part upon the discovery of barrier compositions comprising a mixture of poly(ester) homopolymer or copolymer and poly(vinyl alcohol) or an ethylene/vinyl alcohol copolymer. It has been found that a blend of a polyester and at least about 10% by weight of poly(vinyl alcohol) or an ethylene/vinyl alcohol copolymer, containing greater than about 61 weight per cent or 50 mole per cent of vinyl alcohol, provides a barrier packaging material with optimized gas permeability and moisture-vapor transmission.

Poly(ester) materials, particularly those which are characterized by combination of diols with terephthalic acid, such as poly(ethylene terephthalate), are typically moderate in their permeabilities to oxygen and moisture. Other copolyesters utilizing terephthalic and isophthalic acids with diols or mixtures thereof are also moderate to fair in their gas barrier properties. These particular materials

may be formed from the free acid and a particular glycol, more notably ethylene or butylene glycol, or have been known to be formed through the condensation of phthalate esters with glycols resulting in a thermoplastic material having terminal carboxyl and hydroxyl groups. Examples of these polymers are poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene terephthalate/isophthalate), and poly(ethylene glycol/cyclohexane dimethonal/terephthalate). Copolymers with other phthalic acids are also covered by this invention. A particularly preferred poly(ester) contains alternating units of terephthalic acid and ethylene glycol. This polyester is well known in the textile fibre, film and plastic bottle industries and usually possesses an intrinsic viscosity in the range of .55 to 2 deciliters. The subject polyesters can result from the copolymerization of terephthalic/isophthalic or phthalic acid or an ester derivative with a glycol such as ethylene glycol, propylene glycol, butylene glycol, cyclohexane dimethanol, neopentyl glycol, pentandiol and the like. Other aromatic acids may be used in place of the phthalic acids, such as benzophenone dicarboxylic acid, cyclopentane dicarboxylic acid, diphenylsulfone dicarboxylic acid, diphenylmethane dicarboxylic acid, propylene bis(phenyl carboxylic acid), diphenyloxide dicarboxylic acid and other aromatic diacids. Other polyesters include poly(tetramethylene terephthalate), poly(cyclohexane dimethanol terephthalate), polyethylene dibenzoate, copolyesters of terephthalic acid, an aliphatic dicarboxylic acid and a glycol, etc. Other dicarboxylic acids from which the resins can be derived are dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, brassylic acid,

thapsic acid, diethylsuccinic acid, isophthalic acid, terephthalic acid and hemimellitic acid. Thus, the term "poly(ester)" as used herein is intended to cover at least condensation products of the mentioned acids and polyols.

5 Poly(vinyl alcohol), or more simply "PVA" herein, is usually made by hydrolysis of poly(vinyl acetate), and can be obtained commercially with varying degrees of hydrolysis. The resulting polymers are copolymers of vinyl alcohol and vinyl acetate with contents of vinyl  
10 alcohol in excess of 80 weight per cent. The ethylene/vinyl alcohol copolymers, or more simply "EVAL" herein, can be purchased or converted by hydrolysis to suitable ethylene/vinyl alcohol copolymers. The polymers described herein are hydrolyzed ethylene/vinyl alcohol  
15 copolymers or vinyl alcohol homopolymers, containing up to 10 per cent by weight residual vinyl acetate. Vinyl alcohol copolymers containing greater than 50 per cent vinyl alcohol as a copolymerizate can be converted into films with outstanding gas barrier resistance. Normally,  
20 they are unsatisfactory because of their poor sensitivity to moisture. We describe herein how the moisture-vapor deficiency is remedied by blending the totally hydrolyzed poly(vinyl alcohol) or ethylene/vinyl alcohol copolymers with a polyester, such as poly(ethylene terephthalate),  
25 various copolymers, and other terephthalate polymers.

One embodiment of this invention uses a three component system of poly(ester), poly(vinyl alcohol) or a copolymer and plasticizer. Adding plasticizer usually tends to increase permeability of other polymer blends to oxygen.  
30 However, in the subject blends, such oxygen permeability occurs to a lesser degree than might be expected. Other polymer systems usually begin to lose barrier resistance to oxygen when levels of 5-10 per cent plasticizer are incorporated. On the other hand, poly(ester) and  
35 poly(ethylene/vinyl alcohol) copolymer blends decrease

in oxygen permeation only significantly when adding 20 per cent plasticizer to the blend. Similar behaviour has been shown in blends of poly(ester) with vinyl alcohol polymer and a plasticizer. Plasticizers, in these cases, are typically butyl benzyl phthalate, aromatic phosphates and other types of plasticizers well known to the trade for use with poly(vinyl chloride) and polar polymers. Most such plasticizers are esters of phthalic acid.

In another aspect, blends in accordance with this invention can be fabricated into films that are transparent. This is highly desirable for many food packaging applications utilizing film or bottles. If the poly(ester) resins are replaced by other thermoplastic resins, such as poly(ethylene), poly(styrene), poly(propylene) and styrene-acrylonitrile copolymers, the blends show gross incompatibilities, opacity and phase separation, evidenced by a tendency to delaminate and very poor barrier characteristics.

It has also been found that the coextrusion of the blended materials, as an inner barrier layer, provides a composition with extremely high resistance to moisture vapor transmission and significantly low oxygen permeation so as to provide an optimized packaging material. For example, the coextrusion of three layers comprising a polyolefin outer layer, a middle layer containing a blend of poly(ester) and poly(vinyl alcohol) or ethylene/vinyl alcohol copolmer, and a second external layer of polyolefin, provides a composite with extremely low moisture-vapor transmission and oxygen transmission. Permeabilities for these composites show that the thickness of the centre layer is critical to imparting high barrier properties to the three layer coextrudate.

In a broader aspect, compositions of a poly(ester) and a PVA, or their copolymers, have been found to provide excellent barrier materials. Such combinations might have been expected to be incompatible or poor barriers based upon inter-reaction of hydroxyl groups and/or carboxyl groups of such blends. However, it has not been found to be the case. Rather, excellent barrier properties have been achieved. Furthermore, it was considered wholly unexpected that compositions above 10 per cent by weight of ethylene/vinyl alcohol copolymer or vinyl alcohol homopolymer would produce significant decreases in the permeability to oxygen, marked most notably by a sharp drop in permeability proceeding from about 40-50 per cent by weight of an ethylene/vinyl alcohol copolymer with PETG, a poly(ester) copolymer of terephthalic acid, ethylene glycol and cyclohexane dimethanol (known as "PETG"). It has also been discovered that the ratios of poly(ester) and vinyl alcohol homopolymers and copolymers in these compositions are critical in order to obtain the proper balance of low oxygen permeation and low moisture-vapor transmission. Such blends also exhibit desirable mechanical properties, making them suitable for use in films, bottles, sheet materials and other packaging applications. Whereas ratios of components have been found critical for certain blends, it is to be understood that the invention, in its broadest aspect, is not limited to specific ratios for the polymer blends, in general. These and other embodiments will be further understood with reference to the following examples and drawings in which:

Figure 1 is a diagram of the gas permeability of an EVAL and PETG composition of this invention in comparison to a composition of U.S. Patent 4,003,963, and

Figure 2 is a diagram showing the effect of a plasticizer upon the barrier characteristics of an EVAL and PETG blend of this invention.

Example I - Forty parts by weight of an ethylene/vinyl alcohol copolymer containing 18 per cent ethylene and 82 per cent vinyl alcohol, by weight, was blended in a Brabender extruder with 60 parts by weight of a poly(ester) copolymer made from terephthalic acid, ethylene glycol and cyclohexane dimethanol (known as PETG, available from Eastman Chemical). The resin blend was then pressed into a film by compression molding in a heated press. The oxygen permeability was measured as 6.8 cc-mil/100 in<sup>2</sup>/24 hours/atm at 23.9°C/0%R.H. The moisture vapor transmission was 0.5g.-mil/100 in<sup>2</sup>/24 hours at 23.9°C/50 per cent R.H.

A complete series of varying ethylene/vinyl alcohol (EVAL) copolymers with PETG, by weight, exhibited the oxygen permeability and moisture-vapor transmission shown in Figure 1. The poorer permeability of the poly(ester) is enhanced, as the EVAL is added, in an unexpected manner, showing a sharp drop in the range of about 40-50 per cent EVAL. A plot of an unoriented PVC/ethylene-vinyl alcohol copolymer from the data in Table I of U.S. Patent No. 4,003,963 shows a totally different behaviour than this embodiment.

Example II - Twenty-five parts by weight of an ethylene/vinyl alcohol copolymer containing 18 per cent ethylene and 82 per cent vinyl alcohol, by weight, was blended in a Brabender extruder with 75 parts by weight of a poly(ester) copolymer made from terephthalic acid, ethylene glycol and cyclohexane dimethanol (known as PETG, available from Eastman Chemical). The resin blend was then pressed into a film by compression molding in a heated press. The oxygen permeability measured 14 cc-mil/100 in<sup>2</sup>/24 hours/atm at 23.9°C. The moisture-vapor transmission was 1.3g-mil/100 in<sup>2</sup>/24 hours at 23.9°C/50 per cent R.H.

Another sample was made in which the ethylene/vinyl alcohol copolymer was replaced by fully hydrolyzed



poly(vinyl alcohol) (PVA). After pressing this sample into a film, the oxygen permeability and moisture-vapor transmission results obtained are shown in Table I. The blending of PVA at this level showed a further decrease in oxygen permeability and a slight increase in moisture-vapor transmission, showing that both PVA and EVAL are equally effective in providing a gas barrier with no significant deterioration in the moisture-vapor transmission.

TABLE I

POLYMER BLEND, WT. %			OXYGEN PERMEATION	MOISTURE-VAPOR TRANSMISSION
			(cc) (mil)	(g) (mil)
PEIG	EVAL	PVA	(100 in <sup>2</sup> ) (24 Hrs) (atm) (23.9°C 0% R.H.)	(100 in <sup>2</sup> ) (24 Hrs) (72°F, 50%R.H.)
75	25		14	1.3
75		25	10	2

The use of plasticizers of various types and at various concentrations showed little change in the transport properties as shown in Table II. The ability to plasticize PETG was surprising and particularly to see that the plasticized blends retained the same oxygen permeation using as much as 10-15 per cent plasticizer (Figure 2). SANTICIZER 160 and 141, are Monsanto trade marks for butyl benzyl phthalate and mixed cresyl diphenyl phosphates, respectively.

TABLE II

Effect of Plasticizer on Oxygen Permeability  
of Poly(ester)/Poly(vinyl alcohol) Blends

Plasticized Polymer Blend, Parts					OXYGEN TRANSMISSION: (cc) (ml)/ (100 in <sup>2</sup> ) (24 Hrs) (atm) 23.9°C, 0% R.H.
Polymer			Plasticizer		
PETG	EVAL	PVA	Santicizer 160	Santicizer 141	
75	25		10		12
70		20	10		8
70		20		10	12

5     Example III - A blend of 25 parts by weight of fully hydrolyzed poly(vinyl alcohol), such as Air Products, VINL-125, with 75 parts by weight of PETG was compared to a similar blend in which 25 parts PVA was blended with 75 parts by weight of poly(ethylene-terephthalate) (PET) with an intrinsic viscosity of 0.55 dl. The blends were pressed into films. The oxygen permeability of the films are shown in Table III.

TABLE III

OXYGEN PERMEABILITY OF TWO POLYESTERS  
WHEN BLENDED WITH POLY(VINYL ALCOHOL)

Polymer Wt. %	$P_{O_2}$ (23.9°C, 0% R.H.) (cc) (mil) <hr/> (100 in <sup>2</sup> ) (24 hrs) (atm)	$P_{H_2O}$ (23.9°C, 50% R.H.) (g) (mil) <hr/> (100 in <sup>2</sup> ) (24 hrs)
75 PET 25 PVA	5.3	1.3
75 PETG 25 PVA	10	2.0

Example IV - Coextruded films were made, using the three layer configuration of:

(a) Outer layer - ethylene/vinyl acetate copolymer, containing 2 per cent vinyl acetate by weight (EVA, 2% VA)

5 (b) Middle layer - a blend of 50 parts by weight each of PETG and EVAL

(c) Outer layer - same as (a)

10 Table IVa shows the effect of the 50/50 PETG/EVAL blend and varying its thickness on the oxygen permeability and moisture-vapor transmission of these films. The data show that increasing the thickness as a per cent of total thickness decreases the oxygen permeability, but does not significantly change the moisture-vapor transmission.

15 The data in Table IVb, for a similar three layer film, using an 18 per cent ethylene/82 percent vinyl alcohol EVAL as the centre layer, show the same trend as that demonstrated by the poly(ester)/EVAL blend. The oxygen transmission data for the EVAL three layer film are only slightly less than those of the 50/50 EVAL-poly(ester) blend.

TABLE IV

IV a.

Multilayer Structure Thickness, Mils.			Oxygen Transmission	Moisture-Vapor Transmission
Outer Layer	Center Layer	Inner Layer	cc 100 in <sup>2</sup> 24 hrs atm	g 100 in <sup>2</sup> 24 hrs (23.9°C, 50% R. H.)
EVA (Chemplex 1045) 2% VA	Blend 50% PETG + 50% EVAL	EVA (Chemplex 1045) 2% VA	(23.9°C, 0% R. H.)	
1	0.2	1	0.94	0.042
1	0.4	1.2	0.6	0.032
0.7	0.8	0.7	0.2	0.036



TABLE IV

IV b.

Multilayer Structure Thickness mils			Oxygen Transmission cc 100 in <sup>2</sup> /24 hrs/atm.	Moisture- Vapor Transmission g 100 in <sup>2</sup> /day
Outer Layer	Center Layer	Inner Layer		
EVA (Chemplex 1045) 2% VA	100% EVAL	EVA (Chemplex 1045) 2% VA	23.9°C, 0% R.H.	23.9°C 50% R.H.
1	0.2	1	0.6	0.044
1	0.4	1	0.36	0.019
0.7	0.9	0.7	0.1	0.024

Referring to Tables IVa and IVb, the coextrusion of the blended materials as an inner barrier layer provides a composition with extremely high resistance to moisture-vapor transmission and significantly low oxygen permeation so as to provide an optimized packaging material. For example, the coextrusion of three layers comprising a polyolefin outer layer, a middle layer containing a blend of poly(ester) and poly(vinyl alcohol) or ethylene/vinyl alcohol copolymer, and a second external layer of polyolefin, provides a composite with extremely low moisture-vapor transmission and oxygen transmission. Permeabilities for these composites are shown in Table IV, as a function of the thickness of the barrier layer, showing that the thickness of the centre layer is critical to imparting high barrier properties to the three layer coextrudate.

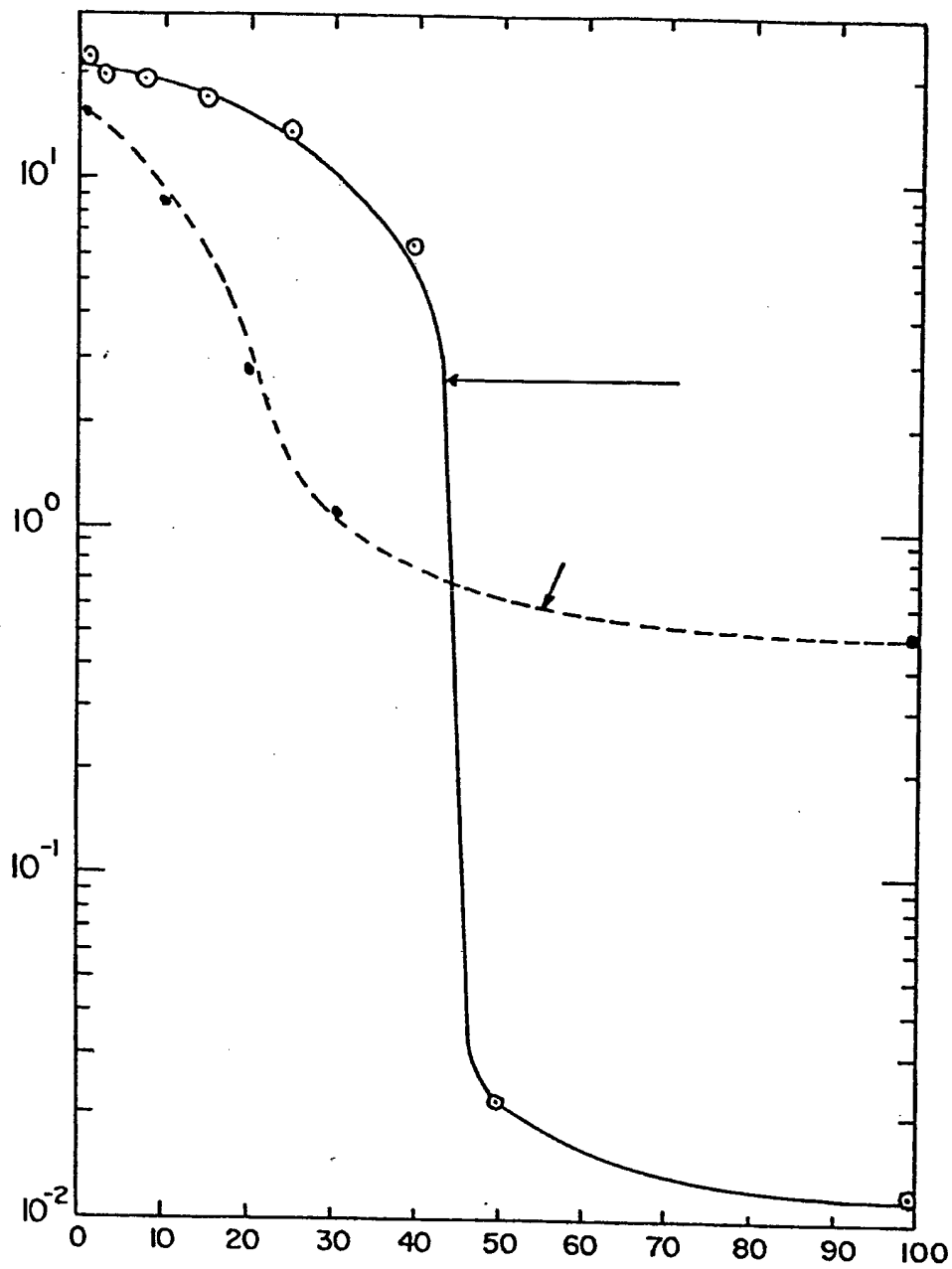
## CLAIMS:

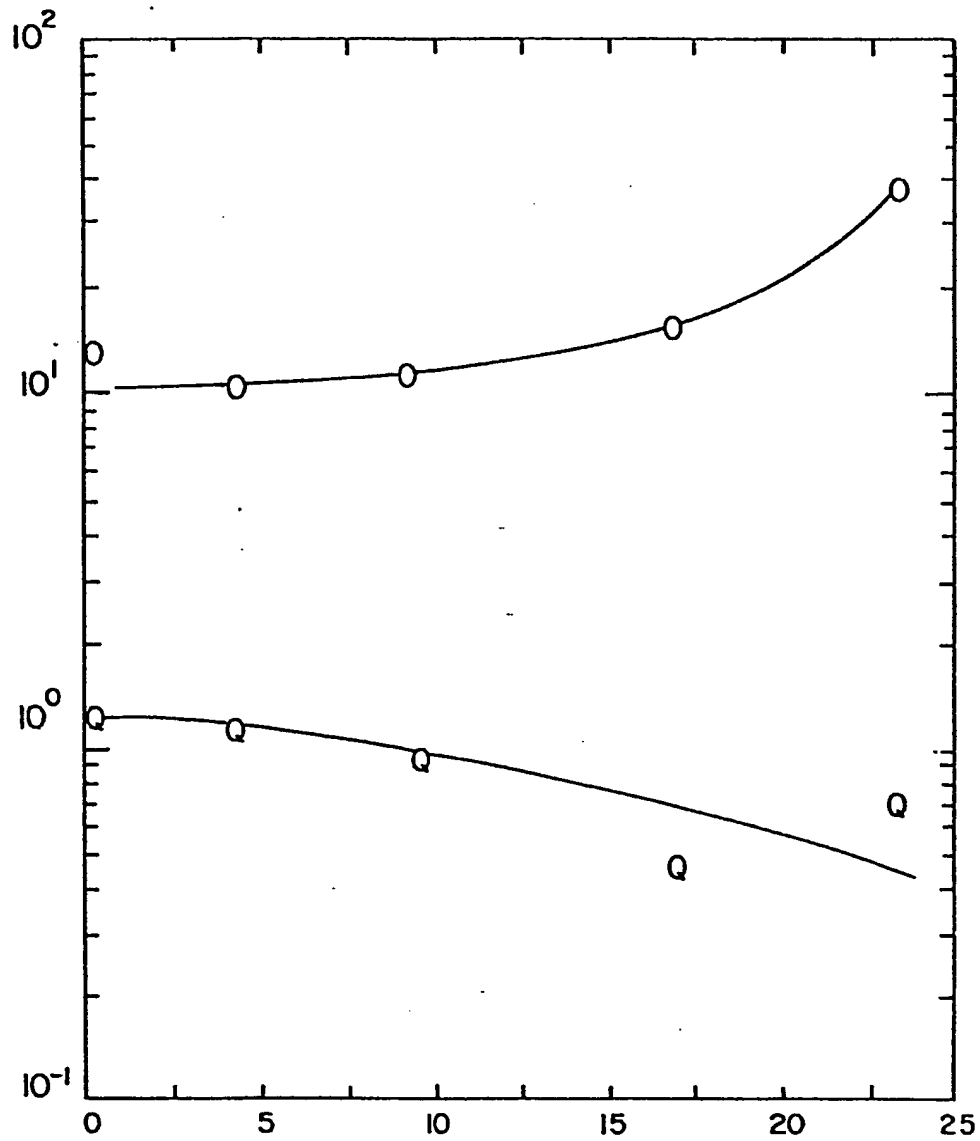
1. A composition for gas and moisture barrier materials comprising a blend of
  - (a) a polymer selected from the group consisting of a poly(ester) and copolymers thereof, and
  - (b) a polymer selected from the group consisting of poly(vinyl alcohol) and copolymers thereof.
2. The composition of claim 1 wherein the poly(ester) is a polymer of a dicarboxylic acid and a polyol.
3. The composition of claim 2 wherein said acid is a terephthalic acid.
4. The composition of claim 2 wherein the poly(ester) is a polymer of terephthalic acid and cyclohexane dimethanol.
5. The composition of claim 2 wherein the poly(ester) is a polymer of terephthalic acid, isophthalic acid and a polyol selected from the group of butane diol and ethylene glycol.
6. The composition of Claim 5 wherein the polymer further includes cyclohexane dimethanol.
7. The composition of Claim 5 wherein said polymer further includes a poly(tetramethylene glycol).
8. The composition of claim 2 wherein said polyol is a polyether polyol.
9. The composition of claim 1 wherein the poly(ester) is selected from the group consisting of poly(ethylene terephthalate) and poly(butylene terephthalate).
10. The composition of claim 1 wherein said copolymer (a) is made from terephthalic acid, ethylene glycol and cyclohexane dimethanol.
11. The composition of claim 10 wherein said poly (vinyl alcohol) copolymer is poly(ethylene/vinyl alcohol) in an amount from at least about 40 per cent by weight

12. The composition of claim 1 wherein said polyvinyl alcohol or copolymer thereof is present in an amount of at least about 10 per cent by weight of said polyester and the polyester is less than about 90 per cent by weight of the blend.
13. The composition of claim 12 wherein said polyvinyl alcohol or copolymer thereof has a weight per cent of vinyl alcohol greater than about 60 per cent.
14. The composition of claim 1, 9 or 10 wherein said polyvinyl alcohol copolymer is poly(ethylene/vinyl alcohol).
15. The composition of claim 1 wherein the polyvinyl alcohol or copolymer contains vinyl acetate groups in an amount of less than 10 per cent by weight of the composition.
16. The composition of any one of the preceding claims further comprising a plasticizer for the polymer blend in an effective plasticizing amount.
17. The composition of claim 16 wherein said plasticizer is an ester of phthalic acid.
18. A barrier material comprising the polymer blend defined in anyone of the preceding claims fabricated into a structural layer.
19. A barrier material comprising a polymer blend defined in anyone of claims 1 to 18 fabricated into a structural layer and further comprising an additional structural layer consisting essentially of another thermoplastic polymer.
20. The barrier material of claim 19 wherein said other thermoplastic polymer is selected from the group consisting of a polyolefin, a polyvinyl chloride polymer and copolymers thereof.
21. The barrier material of claim 1 comprising a composition according to any one of claims 1 to 17 which is extrusion coated onto a porous substrate for decreasing the moisture and gas permeability of the substrate.

22. The barrier material of claim 21 wherein said substrate is selected from the group consisting of a paper and a nonwoven fabric material.

23. A container formed from a layer of barrier material defined in claim 18 when dependant upon claims 1, 9, 10, 11, 13 or 16.

*Fig. 1*



*Fig. 2*



European Patent  
Office

# EUROPEAN SEARCH REPORT

0019438

Application number

EP 80301534.6

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	GB - A - 1 441 071 (NIPPON GOHSEI KAGAKU KOGYO KABUSHIKI KAISHA) + Totality + --	1-3,5, 7,8,11- 16,18	C 08 L 67/02 C 08 K 5/12 C 08 J 5/18 B 32 B 27/36 B 32 B 27/08 B 32 B 27/10 B 65 D 65/40// (C 08 L 67/02 C 08 L 29/04)
X	US - A - 3 580 965 (L. BRINKMANN et al.) + Totality + ----	1-6,9, 10,18	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 08 L 67/00 C 08 L 29/00 C 08 K C 08 J B 32 B B 65 D 65/00
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
<div> <div>X</div> <div>The present search report has been drawn up for all claims</div> </div>			
Place of search		Date of completion of the search	Examiner
VIENNA		22-07-1980	KALTENEGGER